Resonance in the Hydrogen Molecule

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IN a recent paper[1] Mueller and Eyring have discussed the normal state of the hydrogen molecule with use of a variation function constructed in the usual Heitler-London manner, except with replacement, for each electron, of the hydrogen-atom function about atom a, $\exp(-Z'r_a/a_0)$, by the more complex function $\phi_a=\exp(-Z'r_a/a_0)\exp(-Z''r_b/a_0)$. The authors call one-electron functions of this sort semilocalized orbitals. They have compared the value of the bond energy calculated for the wave function $\psi=\psi_1(1)\psi_2(2)+\psi_1(2)\psi_2(1)$, where $\psi_1=\phi_a+\lambda\phi_b$ and $\psi_2=\phi_b+\lambda\phi_a$, with those given by the simple atomic orbital method and the molecular orbital method, and have pointed out that there is an improvement to 4.20 ev, from the values 3.76 ev and 3.60 ev, respectively.

However, the improvement over earlier calculations that are comparable in complexity with the calculation of Mueller and Eyring is in fact not great. The Mueller-Eyring variation function that leads to the bond energy 4.20 ev contains three parameters, λ, Z', and Z'', which have been varied to minimize the energy. Nearly twenty years ago Weinbaum[2] carried out a calculation with use of a variation function of the Heitler-London type, plus ionic terms, and plus terms involving a polarizing factor $\cos\vartheta$ (see the discussion given by Pauling and Wilson[3]). In this treatment, also with a variation function containing three parameters, the bond energy was found to be 4.10 ev, only slightly inferior to the value obtained by Mueller and Eyring.

The closeness of the results obtained by Weinbaum and by Mueller and Eyring is not surprising. Two simple ways of introducing polarization of the hydrogen atom orbitals in the discussion of the hydrogen molecule-ion have been used: One of these, by Dickinson,[4] involves the addition of a polarization term containing the factor $\cos\vartheta$, and the other, by Guillemin and Zener,[5] the use of a function like that used by Mueller and Eyring; it was pointed out by Pauling and Wilson[3] (page 333) that the introduction of the factor $\exp(-Z''r_b/a_0)$, with Z'' small (equal to 0.23 in the Guillemin-Zener function) is equivalent to a polarization of the atomic orbital $\exp(-Z'r_a/a_0)$. There is, moreover, a similarity between the parameters found by Weinbaum to minimize the energy for his ionic-polarization function and those reported by Mueller and Eyring. The Weinbaum parameters are $Z'=1.19$, $\sigma=0.07$ (the coefficient of the polarization term), and $c=0.176$ (the coefficient of the ionic terms). The values of the parameters found by Mueller and Eyring (converted into values of Z' and Z'') are $Z'=1.15$, $Z''=0.043$, and λ (the coefficient of the ionic terms) $=0.137$.

Accordingly, Mueller and Eyring have discussed a wave function for the hydrogen molecule closely similar to that discussed by Weinbaum in 1933, in that it contains three parameters, which are a scale parameter, a parameter essentially determining polarization of a hydrogen-atom orbital, and a parameter determining the contribution of ionic structures. Their treatment represents the extension to the hydrogen molecule of the treatment used by Guillemin and Zener in 1929 for the hydrogen molecule-ion, plus the inclusion of ionic terms.

Mueller and Eyring end their paper with a surprising statement about resonance, which reads as follows: "Both atomic and semilocalized orbitals can be interpreted as postulating two resonance states. In the first resonance state, the state of electron one is represented by the one-electron eigenfunction on the left and the state of electron two is represented by the one-electron eigenfunction on the right. In the second resonance state, the positions of the electrons are reversed. On the other [hand?] the 'Heitler-London plus ionic terms' eigenfunction has been interpreted as implying resonance between covalent and ionic states. Using the hydrogen 1s atomic orbitals ($Z=1$), the calculated energy difference between the covalent state $(\phi_a(1)\phi_b(2))$ and the ionic state $(\phi_a(1)\phi_a(2))$ is 67.28 kcal. Using the Maxwell-Boltzmann distribution law, the ratio of the number of ionic systems to the number of covalent systems is $e^{-112.13}$ or approximately 10^{-49}. While physical interpretations involving resonance states of equal energy may be naive, those involving resonance between states of widely different energies are likely to be ridiculous."

This statement by Mueller and Eyring has, of course, no meaning whatever. The nature of the wave function for a hydrogen molecule in its normal state, or in any definitely specified quantum state, is independent of the temperature of the system in which the hydrogen molecule is present, and the Maxwell-Boltzmann distribution law relates only to the distribution of molecules among states in a system at equilibrium at a specified temperature. The numbers given in the above quotation indicate that the authors have made the Maxwell-Boltzmann calculation for the temperature 300°K; neither this temperature nor any other temperature bears in any way on the question of the electronic structure of the normal hydrogen molecule, and the statement made above by Mueller and Eyring about resonance has no validity.[6] In fact, if the Mueller-Eyring wave function for the hydrogen molecule is expanded into a sum of terms, and these terms are investigated individually with respect to their distribution in configuration space for the two-electron system, it is seen that their function may be conveniently described as involving a combination (which may just as well be called resonance as anything else) of a Heitler-London structure of polarized atomic orbitals and ionic structures, the latter being structures which place both electrons in the neighborhood of one of the two nuclei.

* Contribution No. 1664.
[1] C. R. Mueller and H. Eyring, J. Chem. Phys. **19**, 1495 (1951).
[2] S. Weinbaum, J. Chem. Phys. **1**, 593 (1933).
[3] L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., 1935).
[4] B. N. Dickinson, J. Chem. Phys. **1**, 317 (1933).
[5] V. Guillemin, Jr. and C. Zener, Proc. Natl. Acad. Sci. **15**, 314 (1929).
[6] It may be mentioned that this misapplication of the Boltzmann distribution law is not made in the excellent discussion of resonance in the book *Quantum Chemistry*, by Eyring, Walter, and Kimball (John Wiley and Sons, Inc., New York, 1944).

The Photochemical Decomposition of Methylamine*

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THE results of previous investigations of the photochemical decomposition (direct and photosensitized by mercury) of methylamine[1] have shown that hydrogen, ammonia, and a heavy liquid are the most abundant products. The heavy liquid product is of somewhat uncertain composition and may have the formula $CH_2=N-CH_3$[2] or C_2H_3N[3] or it may be a polymer[3] of either of those substances.

The following reactions:

$$CH_3NH_2+h\nu \text{ (or } Hg(^3P_1))\rightarrow CH_3NH+H(+Hg(^1S_0)) \quad (1)$$
$$H+CH_3NH_2\rightarrow CH_3NH+H_2 \quad (2)$$
$$2\,CH_3NH\rightarrow CH_3N{:}CH_2+NH_3 \quad (3)$$

appear to be generally accepted as representing the initial steps, but Wetmore and Taylor assumed that other reactions such as

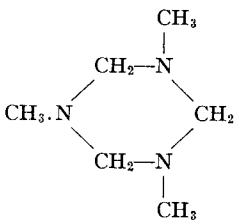
$$H+CH_3NH\rightarrow CH_3NH_2 \quad (4)$$
$$CH_3NH\rightarrow CH_2=NH+H \quad (5)$$
$$CH_2=NH+CH_3NH_2\rightarrow CH_2{:}N.CH_3+NH_3 \quad (6)$$
$$CH_2{:}N.CH_3\rightarrow C_2H_3N+H_2 \quad (7)$$

occur in addition to (1) and (2) and instead of (3).

Reactions (3) and (6) are very complicated for elementary reactions and are therefore rather unlikely processes. Reaction (5), if it occurred at low temperatures, implies that the methyl-

amine radical is very unstable. In view of the data of Phibbs and Darwent[4] on the stability of the rather similar radical CH_2OH, this suggestion appears improbable. The mercury photosensitized reaction of methylamine has been investigated in the hope of obtaining additional information about some of the uncertain points in the above mechanisms.

A heavy liquid was obtained and found to consist largely (about 75 percent) of the compound



i.e., the trimer of $CH_3N{:}CH_2$. This substance was identified by comparison of the physical properties with those of an authentic sample and by the behavior and properties of the derivatives of the known and unknown samples. The other 25 percent of the liquid was composed of a much heavier liquid and unchanged methylamine which had dissolved in the product.

Examination of the uncondensable products showed that (1) hydrogen was the only important lighter product, (2) the rate of production of hydrogen was, initially, independent of time, (3) the initial rate was independent of methylamine pressure between 16 and 398 mm, and (4) the initial rate was only slightly affected by temperature between 20°C and 200°C. These experiments were repeated with CH_3ND_2, and the following additional points were established: (5) the composition of the hydrogen was about 66 percent HD, 33 percent H_2, and 2 percent D_2, (6) the composition of the hydrogen did not change with the duration of the experiment or with temperature between 25° and 200°C. Some experiments with CD_3NH_2 of uncertain purity gave 70 percent HD, 30 percent H_2, and very small amounts of D_2.

The foregoing results (iii and iv) indicate that the hydrogen atoms, produced in reaction (1) disappear by reaction (2) so that reaction (5) is probably of very minor importance. The structure of the liquid product suggests that reaction (7), as written, does not occur and that subsequent dehydrogenation of the product, if this does occur, is probably due to secondary reactions of the product. Points (v) and (vi) show that both of the radicals CH_3NH and CH_2NH_2 are formed, but we are unable to say whether both are formed in reactions (1) and (2), or whether only one is formed in (1) and the other in (2). Some experiments, now in progress, on the reactions of methyl radicals with the deuterated methylamines should give more information about these reactions.

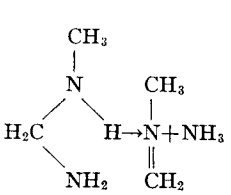
If our conclusions are correct, then the formation of the substance $CH_3N{:}CH_2$ may be explained logically without the necessity of postulating reactions of the type of (3) or (6), since the recombination of those radicals would be expected to yield

$$CH_3.NH.NH.CH_3 \quad (I), \qquad CH_3NH.CH_2.NH_2 \quad (II),$$

and

$$NH_2.CH_2.CH_2.NH_2 \quad (III).$$

Compound II contains one amino group and one substituted amino group attached to the same carbon atom and may be expected to be unstable and to decompose readily into $CH_3N{:}CH_2$ and ammonia



The methyl methyleneimine polymerizes to give the liquid product. It is not surprising that both radical should be produced in these reactions (contrast methyl alcohol)[4] since the C—H and N—H bonds are probably very similar, whereas the O—H bond in methyl alcohol is significantly stronger than the C—H bonds.

Repeated efforts to detect compounds (I) and (III) have proved negative. It must be then concluded that the unlike radicals tend to recombine more readily than do the like radicals, although the reason for this is not clear.

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† N.R.C. Postdoctoral Fellow (1950–52).
[1] W. A. Noyes and P. A. Leighton, *The Photochemistry of Gases*, (Reinhold Publishing Company, New York, 1941), p. 382.
[2] H. J. Emeleus and L. J. Jolley, J. Chem. Soc. 1612 (1935).
[3] O. C. Wetmore and H. A. Taylor, J. Chem. Phys. **12**, 61 (1944).
[4] M. K. Phibbs and B. deB. Darwent, J. Chem. Phys. **18**, 495 (1950).

Polyhedral Flames with Hydrogen and Hydrocarbons

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MANTON, von Elbe, and Lewis[1] have discussed the formation of cellular flames on the basis of two approximate theories, namely (1) hydrodynamic instability of the combustion front and (2) change of the mixture composition due to differential diffusion. They also present experimental evidence from explosions in bombs to support the latter theory.

During some studies concerning the effects of diluents upon temperatures and flame speeds of premixed combustible mixtures, we have found several mixtures that produce polyhedral flames.[2] These results tend to agree with the diffusion theory. Gaseous fuels and oxygen premixed with helium, argon, and nitrogen were burned above a constant velocity nozzle of one-half inch diameter.[3]

In hydrogen flames with argon or nitrogen making up 60 to 80 percent of the mixture, the usual symmetrical cone of the reaction zone was absent, and the flame consisted of several luminous zones separated by dark regions. The luminous zones were convex

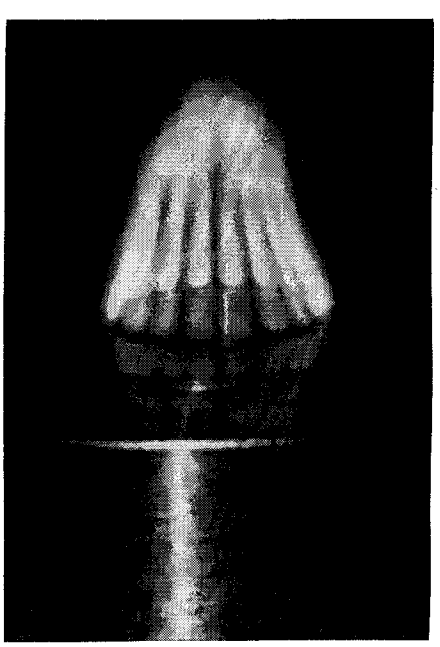

FIG. 1. Flame photograph.